
SIXTH EDITION

Organic Chemistry

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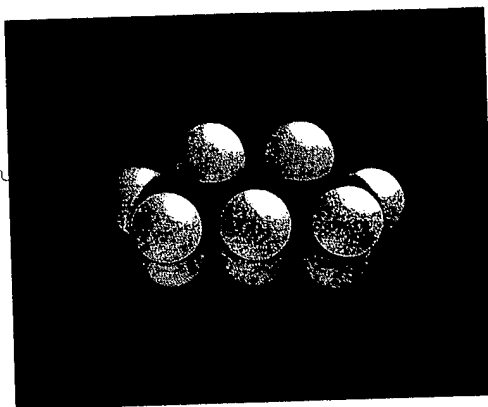
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Alkanes

Free-Radical Substitution

3.1 Classification by structure: the family

The basis of organic chemistry, we have said, is the structural theory. We separate all organic compounds into a number of families on the basis of structure. Having done this, we find that we have at the same time classified the compounds as to their physical and chemical properties. A particular set of properties is thus characteristic of a particular kind of structure.

Within a family there are variations in properties. All members of the family may, for example, react with a particular reagent, but some may react more readily than others. Within a single compound there may be variations in properties, one part of a molecule being more reactive than another part. These variations in properties correspond to variations in structure.

As we take up each family of organic compounds, we shall first see what structure and properties are characteristic of the family. Next we shall see how structure and properties vary within the family. We shall not simply memorize these facts, but, whenever possible, shall try to understand properties in terms of structure, and to understand variations in properties in terms of variations in structure.

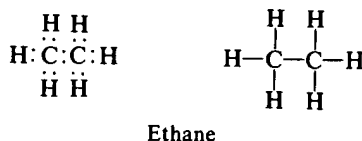
Having studied methane in some detail, let us now look at the more complicated members of the alkane family. These hydrocarbons have been assigned to the same family as methane on the basis of their structure, and on the whole their properties follow the pattern laid down by methane. However, certain new points will arise simply because of the greater size and complexity of these compounds.

But, besides the chemistry of alkanes, we shall be learning something much

more important: basic principles that we shall build on throughout our study. These comparatively simple compounds make an ideal starting point from which to expand our ideas of just what molecular structure is: to see the many ways in which a given set of atoms can be arranged; to find that molecules are not rigid and unchanging, but are flexible and can take on many shapes. Continuing with free-radical halogenation—a simple reaction, free of a complicating solvent—we shall use the concepts of energy of activation and transition state to see why one organic molecule reacts faster than another, and why one part of a molecule reacts faster than another part: a matter that lies at the heart of organic chemistry.

3.2 Structure of ethane

Next in size after methane is **ethane**, C_2H_6 . If we connect the atoms of this molecule by covalent bonds, following the rule of one bond (one pair of electrons) for each hydrogen and four bonds (four pairs of electrons) for each carbon, we arrive at the structure



Each carbon is bonded to three hydrogens and to the other carbon.

Since each carbon atom is bonded to four other atoms, its bonding orbitals (sp^3 orbitals) are directed toward the corners of a tetrahedron. As in the case of methane, the carbon–hydrogen bonds result from overlap of these sp^3 orbitals with the s orbitals of the hydrogens. The carbon–carbon bond arises from overlap of two sp^3 orbitals.

The carbon–hydrogen and carbon–carbon bonds have the same general electron distribution, being cylindrically symmetrical about a line joining the atomic nuclei (see Fig. 3.1); because of this similarity in shape, the bonds are given the same name, σ bonds (*sigma bonds*).

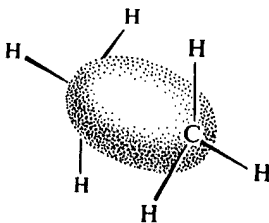


Figure 3.1 Ethane molecule. Carbon–carbon single bond: σ bond.

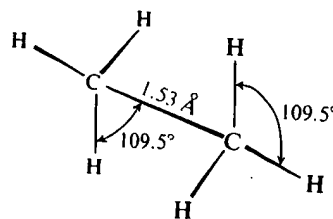
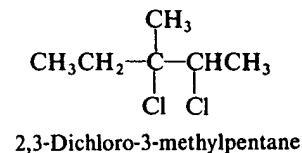
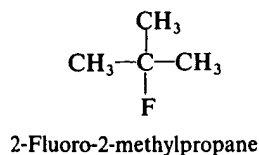
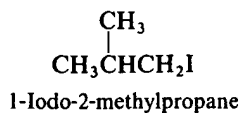
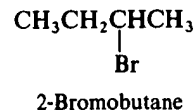
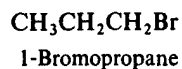
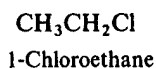


Figure 3.2 Ethane molecule: shape and size.

In ethane, then, the bond angles and carbon–hydrogen bond lengths should be very much the same as in methane, that is, about 109.5° and about 1.10 \AA ,

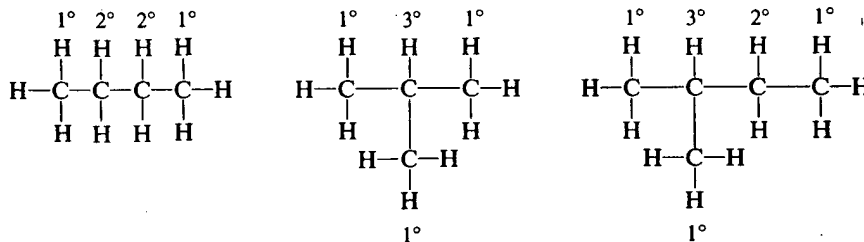


Problem 3.6 Give the IUPAC names for: (a) the isomeric hexanes shown on page 87; (b) the nine isomeric heptanes (see Problem 3.5, p. 87).

Problem 3.7 Give the IUPAC names for: (a) the eight isomeric chloropentanes; (b) the nine isomeric dibromobutanes (see Problem 3.5, p. 87).

3.11 Classes of carbon atoms and hydrogen atoms

It has been found extremely useful to classify each carbon atom of an alkane with respect to the number of other carbon atoms to which it is attached. A **primary** (1°) carbon atom is attached to only one other carbon atom; a **secondary** (2°) is attached to two others; and a **tertiary** (3°) to three others. For example:



Each hydrogen atom is similarly classified, being given the same designation of *primary*, *secondary*, or *tertiary* as the carbon atom to which it is attached.

We shall make constant use of these designations in our consideration of the relative reactivities of various parts of an alkane molecule.

3.12 Physical properties

The physical properties of the alkanes follow the pattern laid down by methane, and are consistent with the alkane structure. An alkane molecule is held together entirely by covalent bonds. These bonds either join two atoms of the same kind and hence are non-polar, or join two atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non-polar or very weakly polar.

As we have seen (Sec. 1.19), the forces holding non-polar molecules together (van der Waals forces) are weak and of very short range; they act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Within a family, therefore, we would expect that the larger the molecule—and hence the larger its surface area—the stronger the intermolecular forces.

Table 3.3 lists certain physical constants for a number of the *n*-alkanes. As we can see, the boiling points and melting points rise as the number of carbons increases. The processes of boiling and melting require overcoming the intermolecular forces of a liquid and a solid; the boiling points and melting points rise because these intermolecular forces increase as the molecules get larger.

Table 3.3 ALKANES

Name	Formula	M.p., °C	B.p., °C	Relative density (at 20 °C)
Methane	CH ₄	-183	-162	
Ethane	CH ₃ CH ₃	-172	-88.5	
Propane	CH ₃ CH ₂ CH ₃	-187	-42	
<i>n</i> -Butane	CH ₃ (CH ₂) ₂ CH ₃	-138	0	
<i>n</i> -Pentane	CH ₃ (CH ₂) ₃ CH ₃	-130	36	0.626
<i>n</i> -Hexane	CH ₃ (CH ₂) ₄ CH ₃	-95	69	0.659
<i>n</i> -Heptane	CH ₃ (CH ₂) ₅ CH ₃	-90.5	98	0.684
<i>n</i> -Octane	CH ₃ (CH ₂) ₆ CH ₃	-57	126	0.703
<i>n</i> -Nonane	CH ₃ (CH ₂) ₇ CH ₃	-54	151	0.718
<i>n</i> -Decane	CH ₃ (CH ₂) ₈ CH ₃	-30	174	0.730
<i>n</i> -Undecane	CH ₃ (CH ₂) ₉ CH ₃	-26	196	0.740
<i>n</i> -Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	-10	216	0.749
<i>n</i> -Tridecane	CH ₃ (CH ₂) ₁₁ CH ₃	-6	234	0.757
<i>n</i> -Tetradecane	CH ₃ (CH ₂) ₁₂ CH ₃	5.5	252	0.764
<i>n</i> -Pentadecane	CH ₃ (CH ₂) ₁₃ CH ₃	10	266	0.769
<i>n</i> -Hexadecane	CH ₃ (CH ₂) ₁₄ CH ₃	18	280	0.775
<i>n</i> -Heptadecane	CH ₃ (CH ₂) ₁₅ CH ₃	22	292	
<i>n</i> -Octadecane	CH ₃ (CH ₂) ₁₆ CH ₃	28	308	
<i>n</i> -Nonadecane	CH ₃ (CH ₂) ₁₇ CH ₃	32	320	
<i>n</i> -Icosane	CH ₃ (CH ₂) ₁₈ CH ₃	36		
Isobutane	(CH ₃) ₂ CHCH ₃	-159	-12	
Isopentane	(CH ₃) ₂ CHCH ₂ CH ₃	-160	28	0.620
Neopentane	(CH ₃) ₄ C	-17	9.5	
Isohexane	(CH ₃) ₂ CH(CH ₂) ₂ CH ₃	-154	60	0.654
3-Methylpentane	CH ₃ CH ₂ CH(CH ₃)CH ₂ CH ₃	-118	63	0.676
2,2-Dimethylbutane	(CH ₃) ₃ CCH ₂ CH ₃	-98	50	0.649
2,3-Dimethylbutane	(CH ₃) ₂ CHCH(CH ₃) ₂	-129	58	0.668

Except for the very small alkanes, the boiling point rises 20 to 30 degrees for each carbon that is added to the chain; we shall find that this increment of 20–30 degrees per carbon holds not only for the alkanes but also for each of the homologous series that we shall study.

The increase in melting point is not quite so regular, since the intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit into a crystal lattice.

The first four *n*-alkanes are gases, but, as a result of the rise in boiling point and melting point with increasing chain length, the next thirteen (C_5 – C_{17}) are liquids, and those containing 18 carbons or more are solids.

Problem 3.8 Using the data of Table 3.3, make a graph of: (a) b.p. vs. carbon number for the *n*-alkanes; (b) m.p. vs. carbon number; (c) density vs. carbon number.

There are somewhat smaller differences among the boiling points of alkanes that have the same carbon number but different structures. On pages 84 and 87 the boiling points of the isomeric butanes, pentanes, and hexanes are given. We see that in every case a *branched-chain isomer has a lower boiling point than a straight-chain isomer*, and further, that the more numerous the branches, the lower the boiling point. Thus *n*-butane has a boiling point of 0 °C and isobutane –12 °C. *n*-Pentane has a boiling point of 36 °C, isopentane with a single branch 28 °C, and neopentane with two branches 9.5 °C. This effect of branching on boiling point is observed within all families of organic compounds. That branching should lower the boiling point is understandable: with branching the shape of the molecule tends to approach that of a sphere; and as this happens the surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature (Sec. 1.20). Compare the shapes of the isomeric pentanes, for example, as shown in Fig. 3.10.

In agreement with the rule of thumb, “like dissolves like”, the alkanes are soluble in non-polar solvents such as benzene, ether, and chloroform, and are insoluble in water and other highly polar solvents. Considered themselves as solvents, the liquid alkanes dissolve compounds of low polarity and do not dissolve compounds of high polarity.

The relative density increases with size of the alkanes, but tends to level off at about 0.8; thus all alkanes are less dense than water. It is not surprising that nearly all organic compounds are less dense than water since, like the alkanes, they consist chiefly of carbon and hydrogen. In general, to be denser than water a compound must contain a heavy atom like bromine or iodine, or several atoms like chlorine.

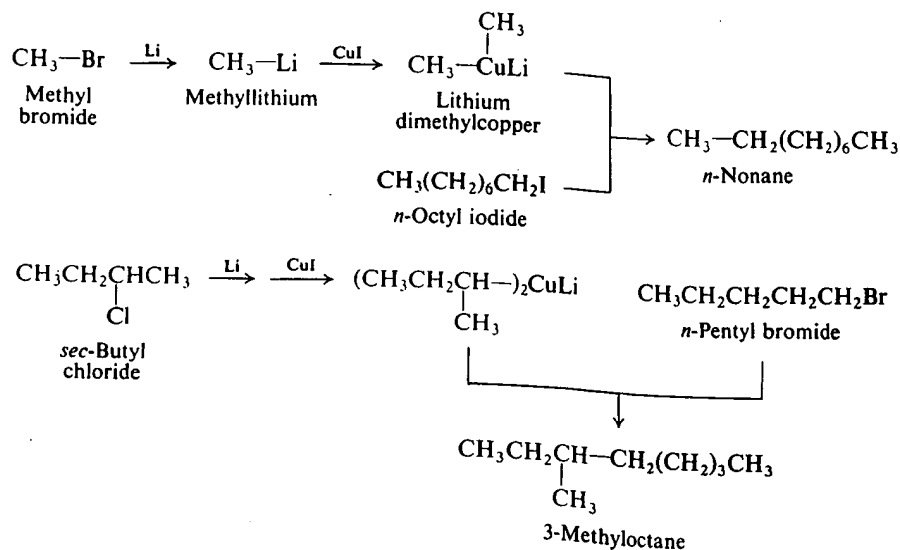
3.13 Industrial source

The principal source of alkanes is **petroleum**, together with the accompanying **natural gas**. Decay and millions of years of geological stresses have transformed the complicated organic compounds that once made up living plants or animals into a mixture of alkanes ranging in size from one carbon to 30 or 40 carbons. Formed along with the alkanes, and particularly abundant in California petroleum, are *cycloalkanes* (Chap. 13), known to the petroleum industry as *naphthenes*.

The other fossil fuel, coal, is a potential second source of alkanes: processes are being developed to convert coal, through hydrogenation, into gasoline and fuel oil, and into synthetic gas to offset anticipated shortages of natural gas.

Natural gas contains, of course, only the more volatile alkanes, that is, those of low molecular weight; it consists chiefly of methane and progressively smaller amounts of ethane, propane, and higher alkanes. For example, a sample taken from a pipeline supplied by a large number of Pennsylvania wells contained

For good yields, $R'X$ should be a *primary* halide; the alkyl group R in the organometallic may be primary, secondary, or tertiary. For example:



The choice of organometallic reagent is crucial. Grignard reagents or organolithium compounds, for example, couple with only a few unusually reactive organic halides. Organosodium compounds couple, but are so reactive that they couple, as they are being formed, with their parent alkyl halide; the reaction of sodium with alkyl halides (*Wurtz reaction*) is thus limited to the synthesis of symmetrical alkanes, $R\text{—}R$.

Organocopper compounds were long known to be particularly good at the formation of carbon-carbon bonds, but are unstable. Here, they are generated *in situ* from the organolithium, and then combine with more of it to form these relatively stable organometallics. They exist as complex aggregates but are believed to correspond roughly to $R_2\text{Cu}^-\text{Li}^+$. The anion here is an example of an *ate* complex, the negative counterpart of an *onium* complex (ammonium, oxonium).

Although the mechanism is not understood, this much is clear: the alkyl group R is transferred from copper, taking a pair of electrons with it, and becomes attached to the alkyl group R' in place of halide ion (*nucleophilic aliphatic substitution*, Sec. 5.7).

Problem 3.11 (a) Outline two conceivable syntheses of 2-methylpentane from three-carbon compounds. (b) Which of the two would you actually use? Why?

3.18 Reactions

The alkanes are sometimes referred to by the old-fashioned name of *paraffins*. This name (Latin: *parum affinis*, not enough affinity) was given to describe what appeared to be the low reactivity of these hydrocarbons.

But reactivity depends upon the choice of reagent. If alkanes are inert toward hydrochloric and sulfuric acids, they react readily with acids like HF—SbF_5 and $\text{FSO}_3\text{H—SbF}_5$ ("magic acid") to yield a variety of products. If alkanes are inert toward oxidizing agents like potassium permanganate or sodium dichromate, most of this chapter is devoted to their oxidation by halogens. Certain yeasts feed happily on alkanes to produce proteins—certainly a chemical reaction. As Professor

M. S. Kharasch (p. 330) used to put it, consider the "inertness" of a room containing natural gas, air, and a lighted match.

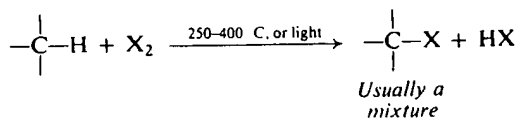
Still, on a comparative basis, reactivity is limited. "Magic acid" is, after all, one of the strongest acids known; halogenation requires heat or light; combustion needs a flame or spark to get it started.

Much of the chemistry of alkanes involves free-radical chain reactions, which take place under vigorous conditions and usually yield mixtures of products. A reactive particle—typically an atom or free radical—is needed to begin the attack on an alkane molecule. It is the generation of this reactive particle that requires the vigorous conditions: the dissociation of a halogen molecule into atoms, for example, or even (as in pyrolysis) dissociation of the alkane molecule itself.

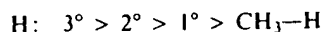
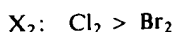
In its attack, the reactive particle abstracts hydrogen from the alkane; the alkane itself is thus converted into a reactive particle which continues the reaction sequence, that is, carries on the chain. But an alkane molecule contains many hydrogen atoms and the particular product eventually obtained depends upon *which* of these hydrogen atoms is abstracted. Although an attacking particle may show a certain selectivity, it can abstract a hydrogen from any part of the molecule, and thus bring about the formation of many isomeric products.

REACTIONS OF ALKANES

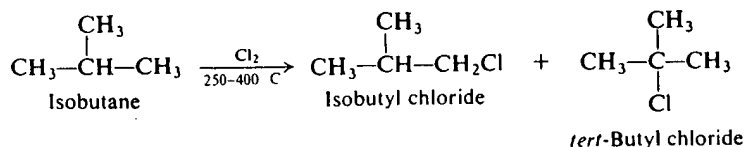
1. Halogenation. Discussed in Secs. 3.19–3.22.



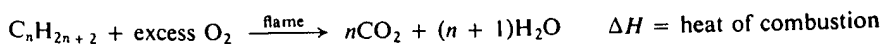
Reactivity



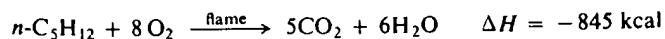
Example:



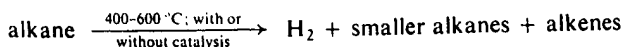
2. Combustion. Discussed in Sec. 3.30.



Example:



3. Pyrolysis (cracking). Discussed in Sec. 3.32.



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